RHEOLOGICAL PROPERTIES AND IMPACT BEHAVIOR
Multi-component Thermoplastic Composites

5th Annual ASM/ESD Advanced Composites Conference/Exposition
Dearborn - September 26, 1989

Stephen Burke Driscoll
Lisa Federico
Daniel Gallagher
Douglas Harrington

The University of Lowell
in Massachusetts

Dr. R.M.V.G.K. Rao
National Aeronautical
Laboratory

Bangalore, India

Introduction:

The steady growth of reinforced plastics/composites has been very encouraging and no slowdown is predicted for the coming decade. In fact new developments in materials, complemented by innovations in processing, will enhance the stature of RP/Cs in the years ahead. One important member of this composite field is thermoplastic sheeting.

Starting with the PPG co-developed AZDEL* polypropylene glass mat product and further enhanced by Allied STX* stampable nylon and Phillip's RYTON PPS a decade ago, Glass Mat Thermoplastics (GMT) now include the recently expanded GE's Technopolymers product line of AZDEL*, AZMET* semicrystalline PET-based sheeting, and AZLOY* amorphous PC/PBT. Also joining the competition is Exxon's TAFFEN* random-chopped glass PP sheeting. BASF has announced plans to introduce its TPC series of nylon and PP impregnated random or unidirectional glass mats.

The developments in the material side of the TPC have been matched by similar innovations in processing. The early 1980's witnessed many developments, including:

1) Yates' development of the ROLL-TRUSION* process, as reported by Driscoll and Plumer (1)

2) the concurrent announcement by ICI for roll-forming PEEK composites

3) other US ARMY-AMMRC funded techniques, such as Madenjian's fluidized bed-coating operation (2)

4) Muzzy et. al., published recently a paper on electrostatic prepregging using LARC-TPI and PEEK (3)

Each composite system and process/fabrication approach has resulted in enhanced performance. The use of hybrids of fillers and reinforcing agents as well as different resins systems (or thermoplastic alloys) as the impregnating matrix allows the materials engineer to build-in selected performance credentials demanded by the design and processing engineers. The scope of this interim report on these thermoplastic composite constructions is to detail what can be done and to report briefly on some selected results.

The ASTM D-20 Committee of Plastics founded ten years ago in this hotel the D 20.10.15 Section on Dynamic Mechanical Properties. In the past decade a family of testing protocols has been authored by representatives of material suppliers, fabricators, and users of plastics materials. The published ASTM documents include:

D 4065	Dynamic Mechanical Properties
D 4092	Glossary of Terms and Definitions
D 4440	Melt Viscosity
D 4473	Cure Behavior of Thermosetts

Projects being balloted include:

X-10-115	Dynamic Tension
X-10-116	Dynamic Three Point Bending
X-10-121	Dynamic Compression
X-10-157	Dynamic Torsion

These documents allow the materials-design-processing engineer to characterize the important rheological properties of a material and to translate this viscoelastic behavior into practical term of design worthiness and processability.

Although an important aspect of composite performance is processability, an equally invaluable assessment of the functional behavior is demanded. This paper will address briefly this second area of interest.

Dynamic mechanical testing of composites is based on a controlled deformation of the material system and measuring the response to that mechanical deformation. The degrees of freedom in rheological testing include the frequency, the temperature, the strain amplitude of deformation, and the time factor.

ASTM cautions very clearly that testing should only be done at very low frequencies in order to avoid masking important transitions. The temperature gradient should also be limited to 3 to 5 C/minute to ensure that the material is indeed at the reference temperature. (The following examples have been tested at low frequencies (1 to 10 radians/second) and thermal ramps of 3 C/minute.)

Experimental:

A Rheometrics Mechanical Spectrometer (Model RMS 605) was used in the forced-oscillatory deformation of torsional samples. The strain amplitude (typically below 0.5%) is a function of the sample geometry. Although the torsional geometry was selected, dynamic three-point bending would have been equally appropriate. In fact, using both would allow easy determination of Poisson's ratio.

Analogous to the sensitivity of thermoset composites to resin type, curing agent, fiber reinforcement / direction and aging problems, TPC's are similarly susceptible to the inherent variations in the polymer's architecture (molecular weight, its distribution, and branching) as well as alloy/blend compositions. These material-dependent features can be easily monitored using ASTM D 4440 (dynamic, frequency sweep test mode, parallel plate geometry). (4, 5)

Consequently, the engineer does have a powerful analytical tool for monitoring the material during processing (critical viscosities as a function of processing temperatures) as well as measuring the resultant functional performance of the fabricated product. To illustrate how the fabrication scheme can be used effectively to direct these properties, a series of TPC's was prepared using different symmetrical and asymmetrical assemblies of:

ULTEM* polyetherimide impregnated graphite cloth
VICTREX* PEEK impregnated unidirectional graphite tapes

Sample	Construction
1	All ULTEM*,cloth: AAAAAAA
2	All PEEK* Unidirectional: BBBBBBB
3	A/BBBBB"/A
4	A/BBBBB=/A
5	B"/AAAAA/B"
6	A/B"/A/B"/A/B"/A
7	AAA/B"/AA/B"
8	B"/A/B"B"B"B"/A
9	B=/A/B"B"B=B=/A
10	B"/AA/B"B"/AA
11	B=/AA/B=B=/AA
12	B=B=B=B=B=/B"/B=

Briefly, the data generated by D 4065 and X-10-157 shows several important thermomechanical characteristics:

1. the modulus as a function of temperature

2. various thermal transitions, including Tg and the beta peaks

3. indications of maximum continuous use temperature

4. trends for predicting creep and impact behavior

The following is a summation of these rheological test results:

SHEAR MODULUS, G′ (E10 dynes/sq. cm.)
AS FUNCTION OF TEMPERATURE (C)

Material	RT	100	150	200	300
Unidirectional Epoxy/Graphite Composite					
MD	2.7	2.5	2.3	1.6	0.7
45	1.6	1.5	1.4	1.3	1.0
TD	2.3	1.9	1.4	1.0	0.4
Quasi-	1.8	1.5	1.5	1.3	1.2
ULTEM* Cloth/PEEK* Unidirectional Constructions					
1	1.51	1.14	1.01	0.78	0.04
2	3.53	3.35	2.50	1.10	0.72
3	3.22	2.83	2.40	1.69	0.37
4	1.61	1.45	1.19	0.70	0.09
5	3.50	3.20	2.50	1.69	0.17
6	2.90	2.60	2.30	1.64	0.15
7	3.60	3.30	2.80	1.95	0.16
8	3.00	2.60	1.06	1.30	0.35
9	3.70	3.30	2.50	1.65	0.40
10	2.84	2.50	2.10	1.30	0.17
11	3.50	3.10	2.40	1.60	0.19
12	1.60	1.40	0.66	0.54	0.44

THERMOMECHANICAL BEHAVIOR

	Tg at G" Peak (C)	5 E9 (C)	tan delta peak G"/G′
Unidirectional Epoxy/Graphite Composite			
MD	237	263	0.2932
45	243	300+	0.1220
TD	228	245	0.2640
Quasi-	218	300+	0.0878

ULTEM* Cloth/PEEK* Unidirectional Construction

1	219	210	0.585
2	150	300+	0.132
3	214	230	0.310
4	211	211	0.405
5	214	226	0.468
6	215	224	0.469
7	212	227	0.462
8	210	228	0.258
9	210	234	0.276
10	212	224	0.326
11	211	224	0.324
12	165#	209	0.161

BASED ON THE TAN DELTA PEAK

The second topic to be discussed is the concept of instrumented impact behavior (ASTM D 3763) with emphasis on low-blow, sub-critical impacts. The historical background, rational, and case studies of instrumented impact testing have been documented in ASTM STP 936. (6) Hawkes in 1988 presented a well-documented paper on instrumented impact testing of asymmetrical thermoset composites. (7) Rao, sponsored by a United Nations UNIDO Research Fellowship at The University of Lowell, investigated this same concept, but focused on low-blow impacts of fibrous glass, carbon fiber, and Kevlar*/epoxy composites.

His study of 10- and 20- plies of glass/epoxy and 15-layered Kevlar*/epoxy showed that the deflection and yield energy increased while the percent energy absorbed decreased with available incident energy. For these materials the repeated or multiple-blow impact energy approached the single-blow penetrated energy as the drop height increased.

The deviations between the multiple-blow and single impact event narrowed as the drop height increased. Conversely, the deviations increased at the lower drop heights. Thus, the "Δ H" value can be used either to magnify or narrow the deviations between single and repeated drop height tests. Rao's idea of a FICTITIOUS IMPACT LENS (FIL) is useful for distinguishing between the impact response of various composites, especially those having apparently similar energy absorption capability. Together with the Ductility Index (DI) the drop increment is a powerful testing tool for characterizing impact behavior of composites since the FIL magnifies or contracts the differences in impact response.

Another example of this FIL-concept is the single-blow vs. repeated or multi-impact of selected thermoplastic "stacks". The symmetrical and asymmetrical assemblies were impacted using a Rheometrics Instrumented Impact Tester (Model RDT 5000); the thickness was kept constant and all tests were conducted at ambient conditions.

First, a series of increased thickness and 5-ply assemblies of PC and SMA were impacted. Although the SMA was initially "weaker" this deficiency (as a function of thickness) decreased with increased thickness, and the five-ply constructions exhibited energies of 3030 in-lb for SMA and 3370 in-lb for PC.

Second, a series of symmetrical and asymmetrical constructions were impacted at 8000 ipm:

	Energy (in-lb)
PC/3-SMA/PC	3260
SMA/3-PC/SMA	3220
PC/SMA/PC/SMA/PC	3290
SMA/PC/SMA/PC/SMA	3210
PC/SMA/SMA	3140
SMA/SMA/PC	3080

Since these multi-ply constructions exhibited similar impact behavior, a third series was tested - both at the conventional Izod impacting speed (8000 ipm) and at varying drop heights. The results of these single-blow and repeated drop tests are noted below:

Height (in)	Energy (in-lb) PC/PC/PC	PC/SMA/PC	SMA/PC/PC
5	210	260	250
6	310	310	310
7	400	370	370
8	400	430	430
9	480	470	470
10	540	540	530
11	600	590	580
12	640	630	640
13	680	680	690
14	730	730	760
15	780	800	790
16	850	880	
17	620	900	
18	950		
Cumulative energy:	7430	7590	5820

Single-blow impact energy at 24 inches = 8000 inches/minute

	PC/PC/PC	PC/SMA/PC	SMA/PC/PC
	1210	1220	1230

The conclusions of this preliminary work are:

1. dynamic mechanical testing is a powerful analytical technique for characterizing the rheological properties of thermoplastic composites - especially due to varied, lay-up of directionalized reinforcements.

2. instrumented impact testing has been shown to be effective in discerning significant differences among thermoplastic and thermosetting composites which exhibit apparently similar behavior at isolated conditions

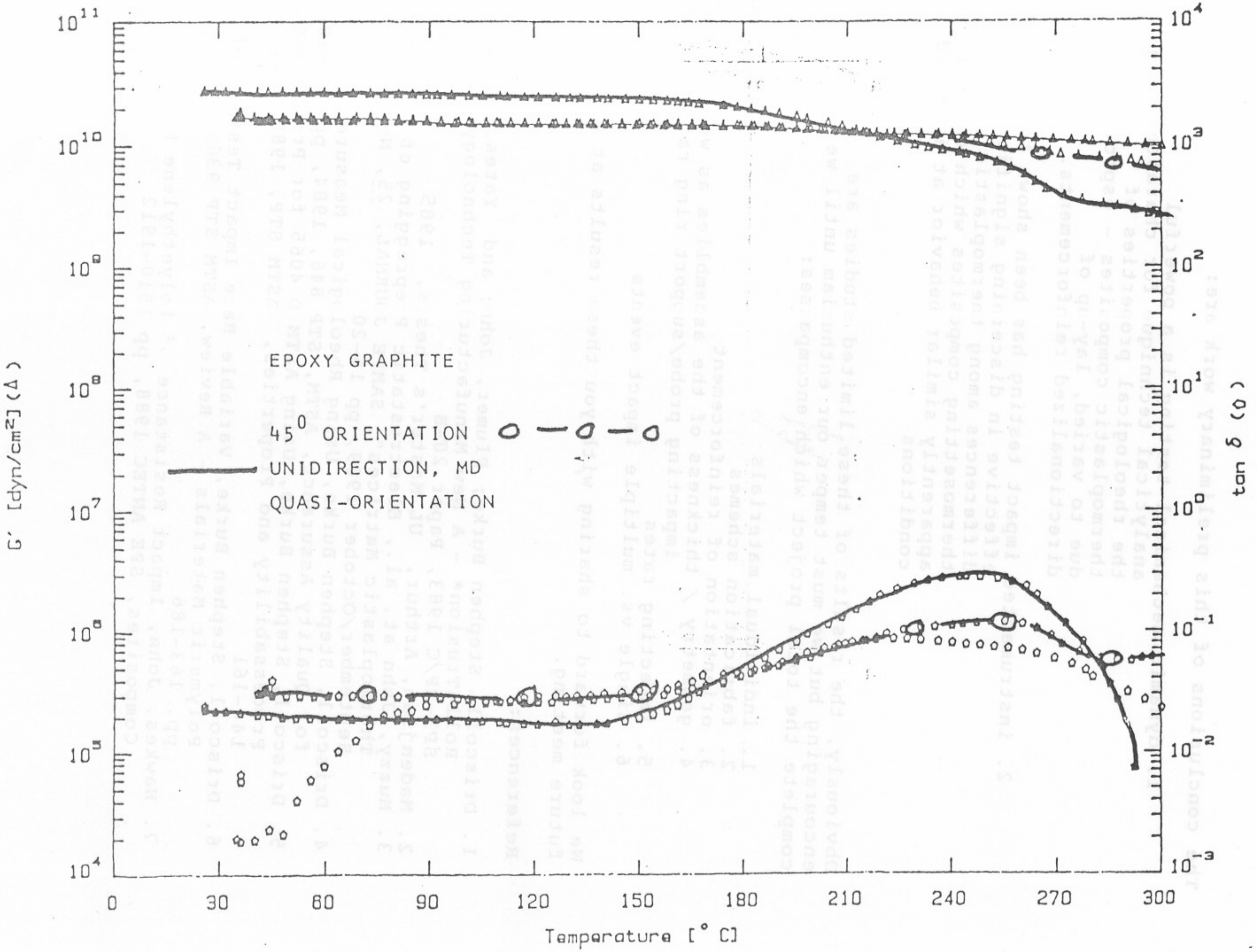
Obviously, the results of these limited studies are encouraging but we must temper our enthusiam until we complete the total project which encompasses:

1. individual materials
2. fabrication schemes
3. orientation of reinforcement
4. geometry / thickness of the assemblies as well as impacting probe/support ring ratio
5. impacting rates
6. single vs. multiple impact events

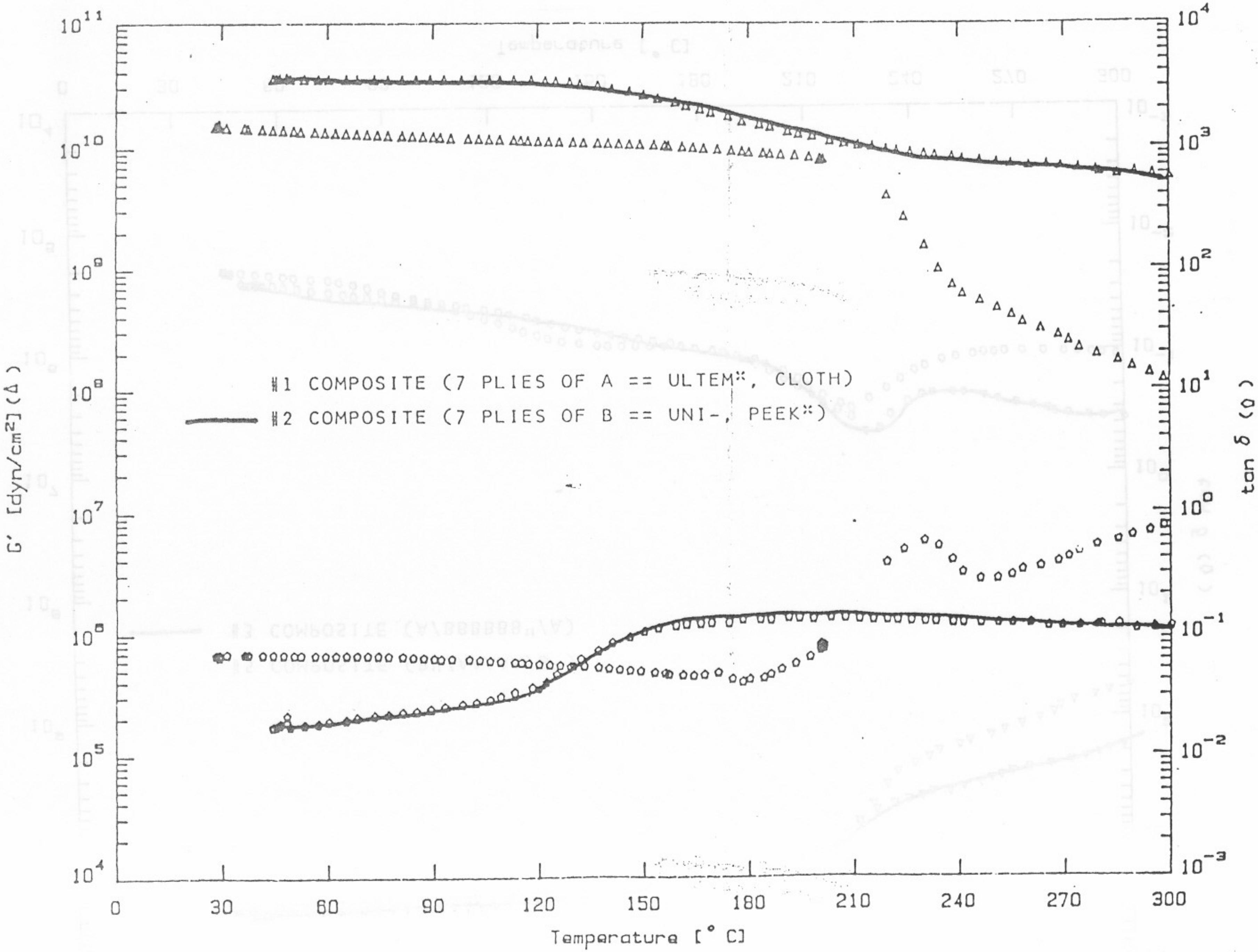
We look forward to sharing with you these results at a future meeting.

References:

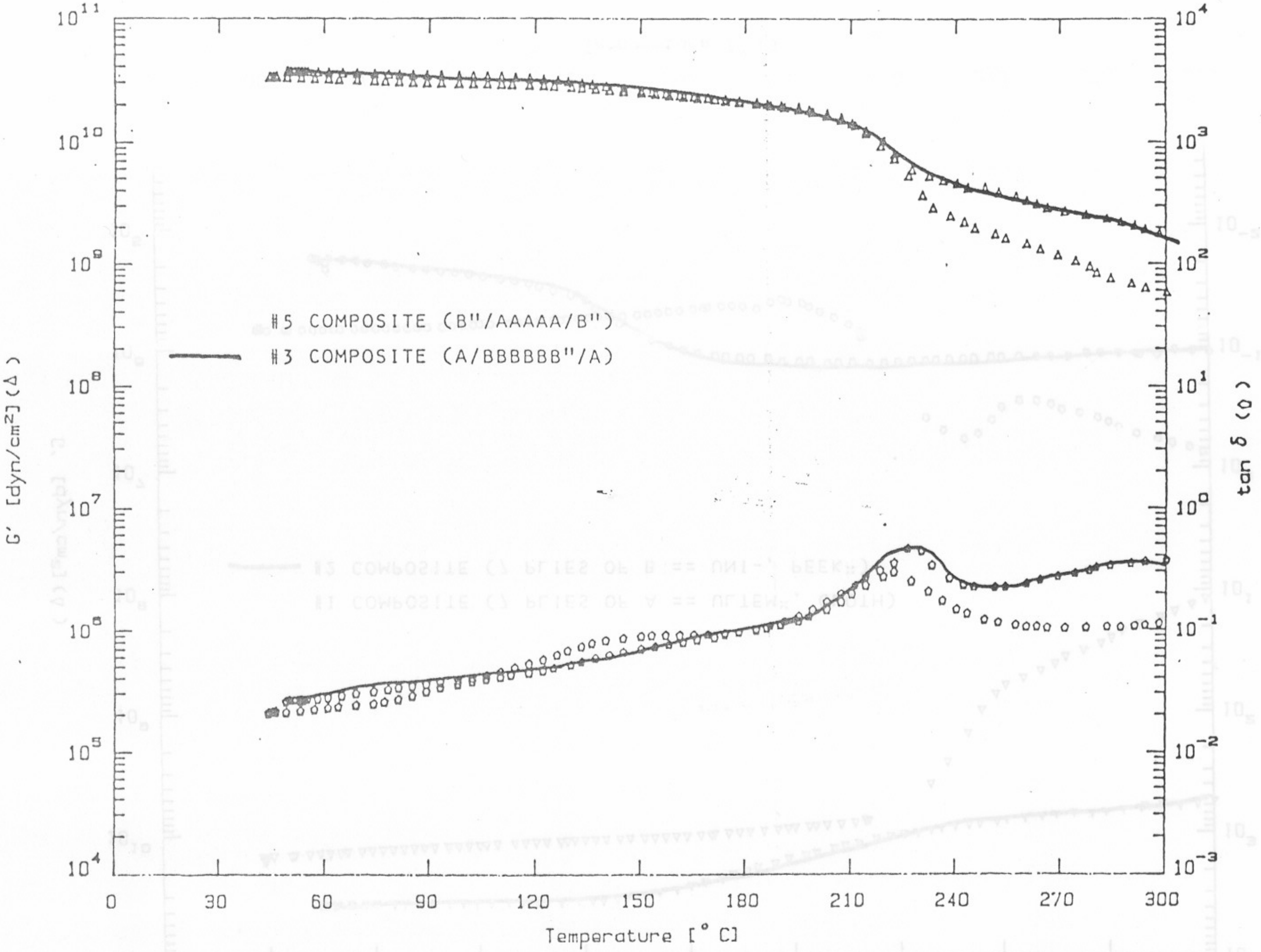
1. Driscoll, Stephen Burke; Plumer, John; and Yates, Mark; Roll-Trusion* - A New Manufacturing Technology, SPI-RP/C 1983, Paper 20-B
2. Madenjian, Arthur, UL Master's Thesis, 1985
3. Muzzy, John at. al., Electrostatic Prepregging of Thermoplastic Matrices", SAMPE JOURNAL, 25, No. 5, September/October 1989, pp 15-20
4. Driscoll, Stephen Burke, Using Rheological Measurements for Quality Assurance, ASTM, STP 846, 1984, pp. 83-102
5. Driscoll, Stephen Burke, Using ASTM D 4065 for Predicting Processability and Properties, ASTM STP, 1985, pp. 144-161
6. Driscoll, Stephen Burke, Variable Rate Impact Testing of Polymeric Materials - A Review, ASTM STP 936, 1986, pp. 163-186
7. Hawkes, John, Impact Resistance of Polyethylene Hybrid Composites, SPE ANTEC 1988, pp 1910-1912



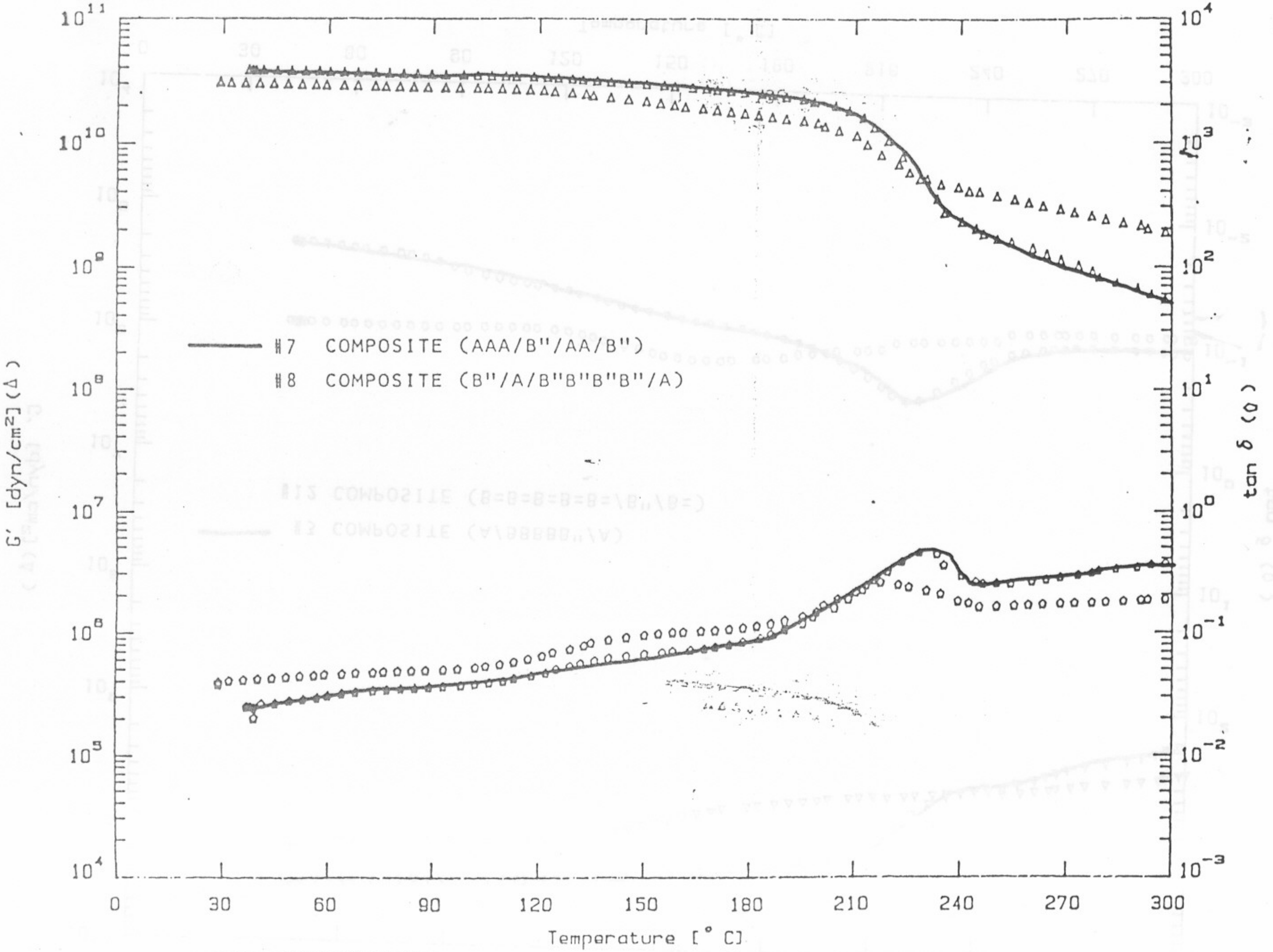
EPOXY GRAPHITE
45 0 ORIENTATION
UNIDIRECTION, MD
QUASI-ORIENTATION
G' [dyn/cm2] (Δ)
tan δ (◊)
Temperature [° C]
0
30
60
90
120
150
180
210
240
270
300



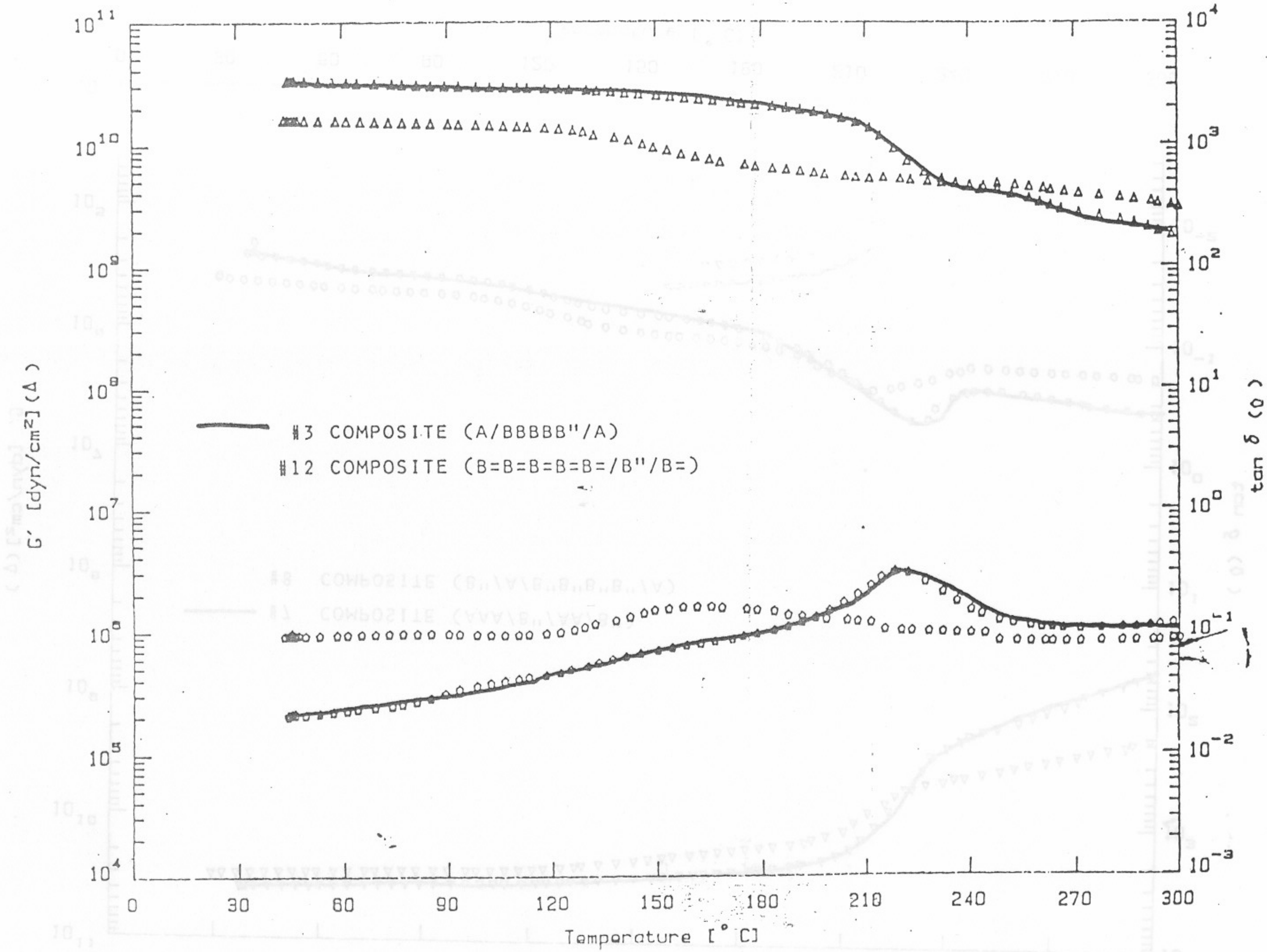
#1 COMPOSITE (7 PLIES OF A == ULTEM*, CLOTH)
#2 COMPOSITE (7 PLIES OF B == UNI-, PEEK*)
G' [dyn/cm²] (Δ)
tan δ (○)
Temperature [° C]



#5 COMPOSITE (B"/AAAAA/B")
#3 COMPOSITE (A/BBBBBB"/A)
G' [dyn/cm²] (Δ)
tan δ (◊)
Temperature [° C]



#7 COMPOSITE (AAA/B"/AA/B")
#8 COMPOSITE (B"/A/B"B"B"B"/A)
G' [dyn/cm^2] (Δ)
tan δ (O)
Temperature [° C]


#3 COMPOSITE (A/BBBBB"/A)
#12 COMPOSITE (B=B=B=B=B=/B"/B=)
G' [dyn/cm²] (Δ)
tan δ (o)
Temperature [°C]
0
30
60
90
120
150
180
210
240
270
300
10¹¹
10¹⁰
10⁹
10⁸
10⁷
10⁶
10⁵
10⁴
10⁴
10³
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³